



Research Article

Removal of Iron(II) Using Intercalated Ca/Al Layered Double Hydroxides with $[\alpha\text{-SiW}_{12}\text{O}_{40}]^{4-}$

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Abstract

Ca/Al layered double hydroxide (LDH) was successfully synthesized by co-precipitation method at pH 11 under room temperature condition then followed by calcination at 800 °C. The synthesized Ca/Al LDH was further intercalated with Keggin ion $[\alpha\text{-SiW}_{12}\text{O}_{40}]^{4-}$ in order to prepare the intercalated form of Ca/Al LDH. The synthesized materials were characterized by X-ray diffraction (XRD) and Fourier transform infrared (FT-IR) and used as an adsorbent for iron(II) removal from the aqueous medium. The adsorption performance was investigated by studying the kinetics and thermodynamic properties of the adsorption process. The results showed that pristine Ca/Al LDH exhibited diffraction peak at 2θ about 20° which corresponds to the layer structure of the LDH material. For the intercalated Ca/Al LDH, the diffraction observed at 2θ around $30\text{-}40^\circ$ indicated that the $[\alpha\text{-SiW}_{12}\text{O}_{40}]^{4-}$ was successfully intercalated into the interlayer space of Ca/Al LDH. Furthermore, the intercalated Ca/Al LDH showed higher adsorption capacity toward iron(II) than the pristine form of Ca/Al LDH. Copyright © 2019 BCREC Group. All rights reserved

Keywords: Layered Double Hydroxides; Iron(II); Keggin Ion; Adsorption

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1. Introduction

The heavy metals pollution has been recognized as tremendous environmental problem in the current decade due to their high toxicity to any living creatures including human being. Moreover, the presence of heavy metals in the environment is hardly degraded naturally with-

out any further treatments. Heavy metal polluted water commonly comes from the industrial process like electroplating, battery manufacture, metal extraction and even household activities [1-3]. These heavy metals are released regularly in various quantities and eventually accumulated in the environment where they were discharged. Heavy metals accumulation more than their allowable threshold will cause numerous detrimental environmental problems due to their high capability to involve in the

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food chain. Consequently, the removal of heavy metals from wastewater is crucial in order to provide a heavy metal free water resource.

Extensive procedures and methods have been applied to remove heavy metals from wastewater. Some of them are coagulation, extraction, membrane filtration, ion exchange, and adsorption [4-8]. Among these established methods, adsorption is considered as one of the most effective methods to remove heavy metals from wastewater due to its high removal efficiency, simple and fast process [9-11]. However, the key factor to the successful adsorption process depends on the performance of the used adsorbent. Currently, numerous adsorbent materials have been tested to remove heavy metal from wastewater like zeolite [12], clays [13], bentonite [14-16], kaolin [17], algae [18], also synthetic layered material (layered double hydroxides) [19-21]. Recently, layered double hydroxides (LDHs) have gained considerable attention to be used as adsorbent due to their versatile metal composition and simple synthesis process.

LDHs are layered compounds, similar to clay and clay minerals, that exhibited positively charged sheets due to the partial isomorphous substitution of the divalent metal cation by the trivalent cation [22]. This material has unique characteristics such as high anion exchange, reactive interlayer space, swelling in water, and colloidal properties [23]. LDH is an inorganic material with the general formula of $[M^{2+}_{1-x}M^{3+}_x(OH)_2]^{x+}(A^{n-})_{x/n} \cdot nH_2O$, where M is divalent and trivalent metal ions, and A^{n-} is interlayer anions with valence n [24]. Some interlayer anions that commonly settle in the interlayer spacing of LDH are nitrate (NO_3^-), chloride (Cl^-), sulfate (SO_4^{2-}), and carbonate (CO_3^{2-}) [25]. The schematic structure of LDH is presented in Figure 1. One of the most interesting properties of LDH is its anion exchange capability that can be utilized to modify its original structure. By changing the original interlayer anion with the larger anion, its interlayer distance and gallery can be expanded, and the surface area can be increased. After that, LDH

can be used as potential inorganic material for various applications like adsorbent, catalyst, biomedical material, and other industrial applications.

Numerous researches on the application of LDH as an adsorbent of heavy metals have been conducted intensively. FeMnMg LDH has been used as an efficient adsorbent to remove Pb(II) ions in water [19]. Removal of Co(II) was effectively conducted using MgAl LDH as adsorbent [26]. While the intercalated MgAl LDH also showed good adsorption properties for removal of heavy metal from wastewater [27]. Considering these reported works, it can be indicated that intercalated LDH is a powerful adsorbent to remove heavy metals from solution. Various anionic intercalants like polyoxometalates were frequently utilized for anion exchange in order to increase the interlayer distance of LDH [28-31]. By intercalating such an anion into the LDH structure, the adsorption of heavy metal will be more effective than the pristine form LDH.

In this research, we reported the intercalation of Ca/Al LDH with Keggin ion $[\alpha-SiW_{12}O_{40}]^{4-}$, and its utilization as adsorbent for iron(II) from aqueous solution. Although the preparation of $[\alpha-SiW_{12}O_{40}]^{4-}$ intercalated Ca/Al LDH has been reported previously, to the best of our knowledge, no work has ever been reported on the application of this material as an adsorbent for iron(II) removal. Furthermore, in order to simplify the intercalation process, we slightly modified the established intercalation method. The adsorption experiments were conducted using a batch system and several factors that influence the adsorption process were studied, including the effect of pH, contact time, concentration of iron(II) solution, and temperature.

2. Materials and Method

2.1 Chemical and Equipment

Chemicals were used as purchased without purification from Merck and Sigma Aldrich, such as: calcium nitrate, iron(III) ni-

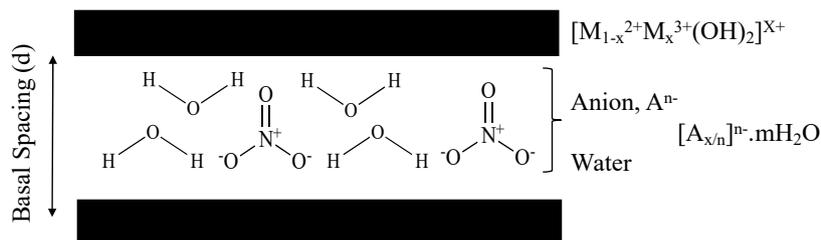


Figure 1. Structure of LDH

trate, iron(II) nitrate, sodium hydroxide, aluminum nitrate, sodium tungsten, and sodium metasilicate. All the used chemicals were analytical grade reagents with >99% purity level. The water that used in the experiment was supplied from Universitas Sriwijaya through ion exchange water purification system at pH 7.

X-Ray powder diffraction analysis was conducted using X-Ray powder diffraction Rigaku Miniflex-600, and the sample was scanned at scan speed $1^\circ \cdot \text{min}^{-1}$. IR analysis was performed using FTIR Shimadzu Prestige-21 at wavenumber $400\text{-}4000 \text{ cm}^{-1}$ using KBr pellet. Analysis of the residual iron(II) concentration was performed using UV spectrophotometer EMC-61PC double beam spectrophotometer using 1,10-phenanthroline as complexing agent.

2.2 Synthesis of Ca/Al LDH

Synthesis of Ca/AL LDH was conducted at pH 11 using co-precipitation method. The procedure was adopted from Granados-Reyes with modification [32]. Calcium nitrate and aluminum nitrate with molar ratio 2:1 ($\text{Ca}^{2+}/\text{Al}^{3+}$) was prepared by adding sodium hydroxide 2 M. The mixtures were stirred at 60°C and pH was adjusted to 11 by slow addition of sodium hydroxide. pH of reaction mixture was adjusted until stable at pH 11 during stirring process. After stable pH, the mixtures were heated using autoclave at 120°C for 2 h. The mixtures were filtered at room temperature and washed with water and dried at 80°C in a laboratory oven (overnight) to form white solid Ca/Al LDH. Ca/Al LDH was calcined at 800°C using muffle furnace for 3 hours in order to know the stability of layer material. Characterization of Ca/Al LDH was performed using XRD and FTIR analyses.

2.3 Synthesis of $\text{K}_4[\alpha\text{-SiW}_{12}\text{O}_{40}] \times n\text{H}_2\text{O}$

Ion $[\alpha\text{-SiW}_{12}\text{O}_{40}]^{4-}$ was synthesized as potassium salt $\text{K}_4[\alpha\text{-SiW}_{12}\text{O}_{40}]$ in an aqueous medium. Sodium metasilicate (11 g) was dissolved into 100 mL of water (solution A). Sodium tungstate (182 g) was dissolved into 300 mL of boiling water (solution B). A solution of 4 M HCl (165 mL) was added drop by drop to solution A over 5 min with vigorous stirring in order to dissolve the local precipitate of tungstic acid. Then solution A was added quickly to solution B followed by adding 50 mL of 4 M HCl. The pH was adjusted to 6. The solution was kept at 373 K for 1 hour. A solution of 1 M sodium tungstate (50 mL) and immediately there-

after, 80 mL of 4 M HCl were added. The solution was filtered after cooling to room temperature. The potassium salt of $\text{K}_4[\alpha\text{-SiW}_{12}\text{O}_{40}]$ was obtained by adjusting pH to around 2 with aqueous 1 M KOH and then solid KCl (50 g) was added. A white precipitate of $\text{K}_4[\alpha\text{-SiW}_{12}\text{O}_{40}]$ was obtained [33]. $\text{K}_4[\alpha\text{-SiW}_{12}\text{O}_{40}]$ was characterized using FT-IR spectrophotometer.

2.4 Intercalation of Ca/Al LDH with $[\alpha\text{-SiW}_{12}\text{O}_{40}]^{4-}$

Ca/Al LDH was intercalated using $[\alpha\text{-SiW}_{12}\text{O}_{40}]^{4-}$ ion by ion exchange method. Potassium salt of $\text{K}_4[\alpha\text{-SiW}_{12}\text{O}_{40}]$ was dissolved with water with a small quantity (solution A). Ca/Al LDH was mixed with a solution of sodium hydroxide (mixture B). Solution A was added into mixture B with gentle stirring under nitrogen condition. The white suspension was formed, and the reaction was performed for 24 hours. The white suspension was vacuum and wash with water. White material was kept at 110°C for 48 hours. Characterization was performed using X-Ray powder analysis and identification using FTIR spectroscopy.

2.5 Stability of Ca/Al LDH under various pH

The synthesized Ca/Al LDH and $[\alpha\text{-SiW}_{12}\text{O}_{40}]^{4-}$ intercalated Ca/Al LDH was contacted with iron(II) solution ($50 \text{ mg} \cdot \text{L}^{-1}$) under vigorous stirring. The mixture was continuously stirred while the pH was adjusted at pH 1-10 by addition of sodium hydroxide or hydrochloric acid solution. Each of adsorbents-iron(II) mixture with different pH condition was analyzed using UV-Visible spectrophotometer and the spectra were recorded at wavelength of 300-700 nm.

2.6 Adsorption Experiment

Adsorption of iron(II) was conducted using Ca/Al LDH as control and intercalated Ca/Al LDH. The adsorption process was studied through adsorption time, concentration of iron(II), and temperature. Variation of adsorption time was adjusted at 10, 20, 30, 40, 50, 60, and 90 min. Effect of initial concentration of iron(II) was varied in concentration 2, 3, 5, 7, 8, 10, and $15 \text{ mg} \cdot \text{L}^{-1}$. Effect of temperature was studied at 30, 40, 50, 60, and 70°C . Filtrate of solution after adsorption was added with 1,10-phenanthroline to form Fe(II)-1,10-phenanthroline complex then further analyzed using UV at λ of 510 nm.

3. Results and Discussion

Ca/Al LDH was characterized by X-Ray powder analysis as shown in Figure 2a. Intensive diffraction was found at 20-50 deg, and small diffraction at 20° - 30° indicated the crystalline phase of Ca/Al LDH due to the presence of anions such as nitrate and carbonate. Nitrate and carbonate anions were found in Ca/Al LDH since the nitrate and carbonate metal salts were used as precursor in the synthesis process. These anions were located on the interlayer space of Ca/Al LDH. The diffraction pattern of Ca/Al LDH after calcined at 800 °C was presented in Figure 1b. Diffraction at 20° - 50° was sharply increased due to the release of water. In this step, mayenite at 53° (640), and 56° (642), and oxides phases were also detected. Ca/Al LDH was detected as layer material as mayenite which has composition $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$. Other phases were detected as Katoite at 17.3° (211), 20.11° (220), 28.5° (321), 31.9° (400), 36.58° (420), 39.3° (431), 44.6° (521), 52.8°

(611), 55.0° (640), and 57.74°(642) [32]. The interlayer distance of Ca/Al LDH was 4.25 Å. Figure 1c showed intercalated Ca/Al LDH with $[\alpha\text{-SiW}_{12}\text{O}_{40}]^{4-}$ ion. Diffraction at 20° was sharper than before intercalation due to insertion of Keggin ion onto interlayer distance of Ca/Al LDH. The interlayer distance was found about 4.41 Å. Slightly changes of interlayer distance after intercalation process was probably due to the diagonal position of Keggin ion toward interlayer. Figure 3 showed that the possibility of Keggin ion onto interlayer Ca/Al LDH with Keggin ion intercalated in diagonal position of interlayer [24]. If position of intercalated Keggin ion with vertical orientation will results interlayer distance with largely value more than 3 Å. In this experiment we found that interlayer distance increases up to 0.16 Å.

FTIR spectrum of Ca/Al LDH was shown in Figure 4a. Sharp vibration at wavenumber 1380 cm^{-1} is assigned as nitrate ion on Ca/Al LDH. The existence of water is shown in vibration at 3410 cm^{-1} with the deep vibration of

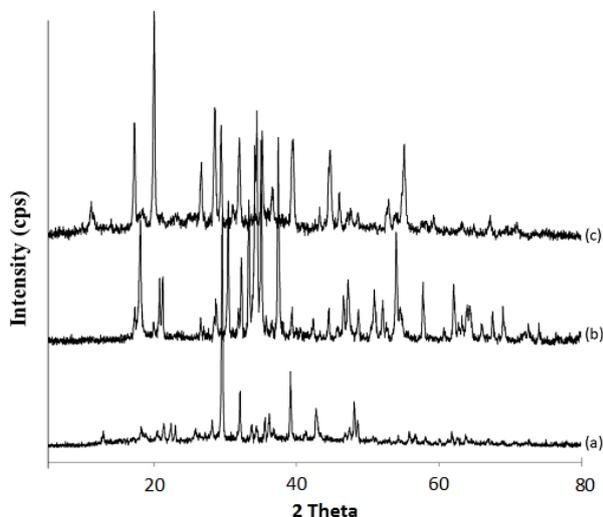


Figure 2. XRD powder pattern of Ca/Al LDH (a), calcination of Ca/Al LDH at 800 °C (b), and intercalated Ca/Al LDH with $\text{K}_4[\alpha\text{-SiW}_{12}\text{O}_{40}]\times n\text{H}_2\text{O}$ (c)

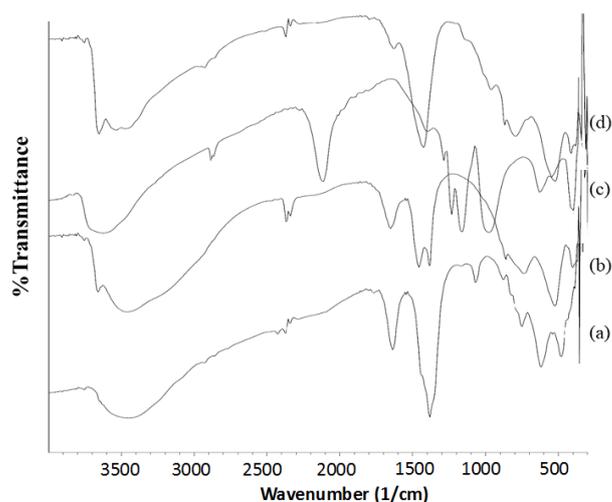


Figure 4. FTIR spectrum of Ca/Al LDH (a), calcination of Ca/Al LDH at 800 °C (b), polyoxometalate $\text{K}_4[\alpha\text{-SiW}_{12}\text{O}_{40}]\times n\text{H}_2\text{O}$ (c), and intercalated Ca/Al LDH with $\text{K}_4[\alpha\text{-SiW}_{12}\text{O}_{40}]\times n\text{H}_2\text{O}$ (d)

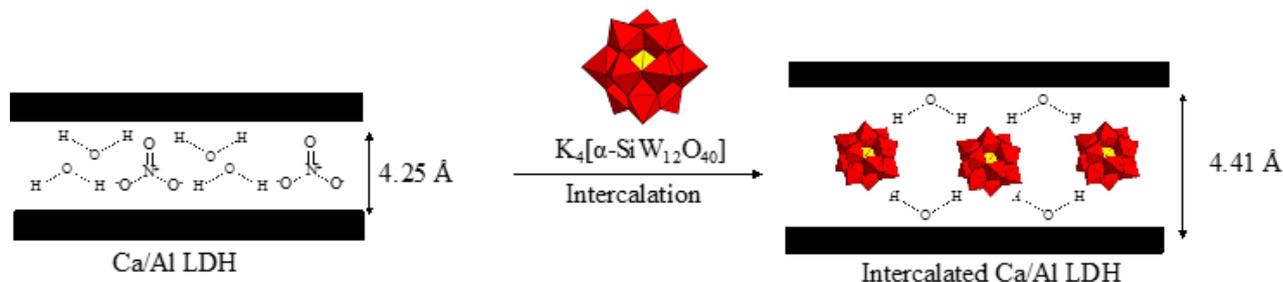


Figure 3. Illustration of intercalation Ca/Al LDH with $[\alpha\text{-SiW}_{12}\text{O}_{40}]^{4-}$

OH. The vibration of nitrate was split into two bands due to the stability of nitrate at high temperature as shown in Figure 4b. Figure 4c shows the unique vibration of Keggin type polyoxometalate of $K_4[\alpha\text{-SiW}_{12}\text{O}_{40}] \times n\text{H}_2\text{O}$ [34]. The unique vibration of $K_4[\alpha\text{-SiW}_{12}\text{O}_{40}] \times n\text{H}_2\text{O}$ appeared at 926 cm^{-1} (n Si-O), 980 cm^{-1} (n W=O), 881 cm^{-1} (n W-Oc-W), and 780 cm^{-1} (n W-Oe-W) [35]. Intercalation of Ca/Al LDH with Keggin ion resulted in spectra in Figure 4d. Intercalation with the large anion to Ca/Al LDH will affect to vibration of nitrate at 1380 cm^{-1} . Thus, vibration at 1380 cm^{-1} after intercalation was broad and sharp.

The stability of Ca/Al LDH and intercalated Ca/Al LDH toward pH of iron(II) was determined using UV-Vis as shown in Figure 5. Figure 5a showed that Ca/Al LDH has the highest absorbance at pH 1. On the other hand, intercalated Ca/Al with Keggin ion has the highest absorbance at pH 2. However, all pH was an acidic condition. These phenomena can be explained because iron(II) was protonated in acid condition and form hydroxides in basic condition. These results were used for adsorption process of iron(II) using both LDH as adsorbents.

Adsorption of iron(II) firstly investigated by adsorption time and the data are presented in Figure 6. Adsorption of iron(II) was slowly at the initial time and increase sharply started at the first 30 minutes. Adsorption of iron(II) on Ca/Al LDH was relatively stable after 60 minutes. On the other hand, adsorption of iron(II) on intercalated LDH was continuously increased. In this case, intercalated Ca/Al LDH has kinetically more active than Ca/Al LDH without intercalation. These phenomena are

probably due to opening layer volume of intercalated Ca/Al LDH.

The data in Figure 6 was used to calculate the adsorption rate constant using Langmuir-Hinshelwood equation [36]. Adsorption rate constant for Ca/Al LDH and intercalated Ca/Al LDH was 4.66 min^{-1} and 10.34 min^{-1} , respectively. These results show intercalated Ca/Al LDH has higher reactivity than Ca/Al LDH before intercalation to adsorb iron(II) from aqueous solution.

Adsorption of iron(II) on Ca/Al LDH and intercalated Ca/Al LDH was continued by the effect of concentration of iron(II) and temperature as shown in Figure 7a-b. Adsorption of iron(II) for both adsorbents show an increase by increasing temperature adsorption. Also, adsorption was increased by increasing concentration of iron(II). These results are generally occurred for adsorption of both for gas and liquid adsorbate in which adsorption capacity increase by increasing temperature. On the other hand, for both Ca/Al LDH and intercalated Ca/Al LDH have higher adsorption capacity at $40\text{ }^\circ\text{C}$ than 60 and $70\text{ }^\circ\text{C}$ at concentration of

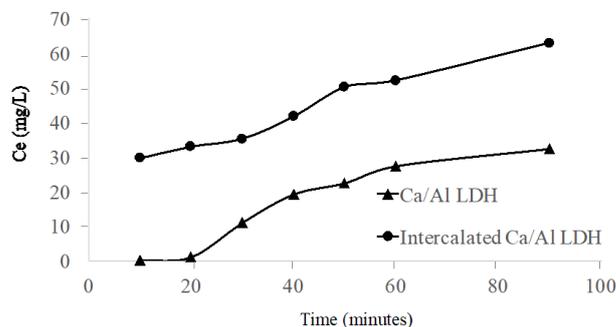


Figure 6. Effect of adsorption time of iron(II)

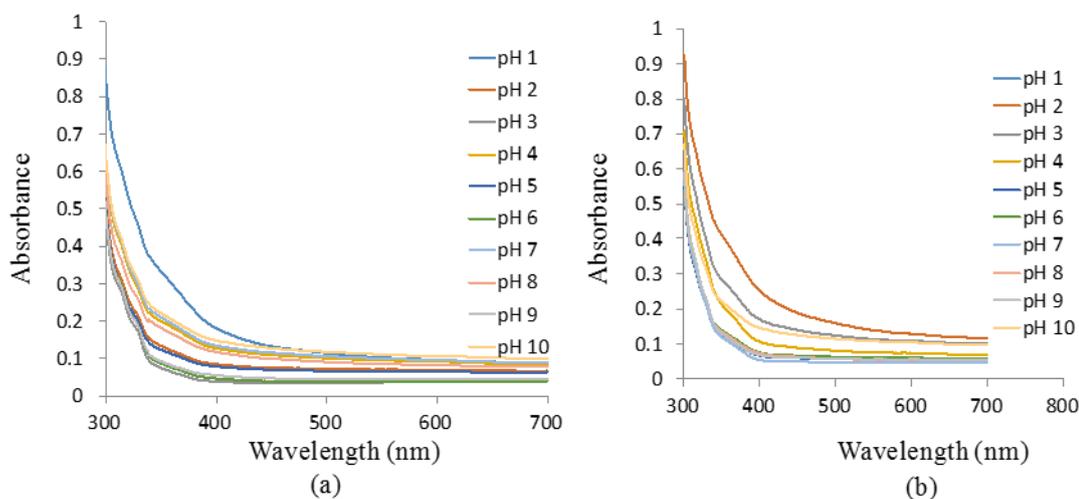


Figure 5. Stability of Ca/Al LDH (a) and intercalated Ca/Al (b) under various pH

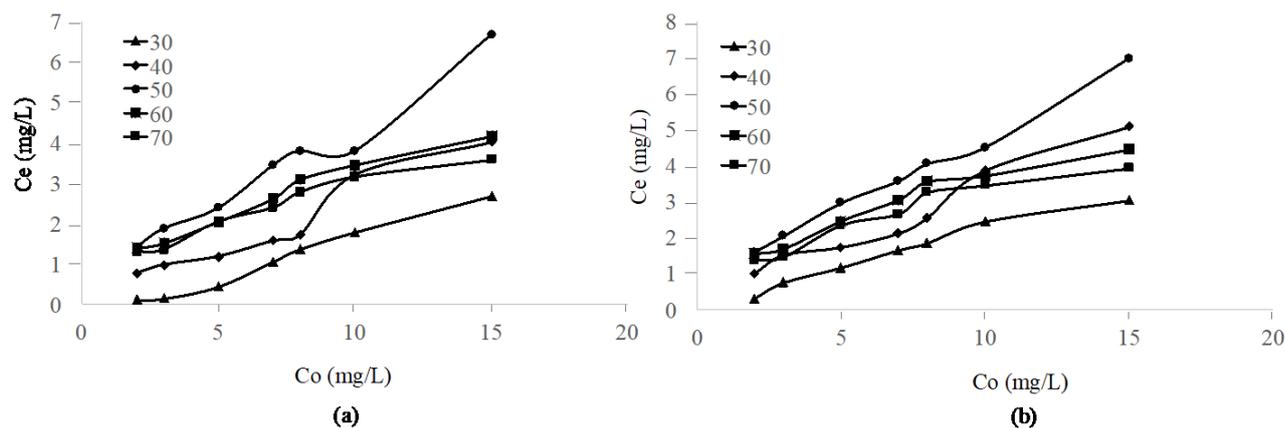


Figure 7. Effect of initial concentration of iron(II) and temperatures of adsorption iron(II) on Ca/Al LDH (a) and intercalated Ca/Al (b)

iron (II) 10 mg.L⁻¹. The anomalies were also found at temperature 50 °C for both Ca/Al LDH and intercalated Ca/Al LDH where adsorption capacity was slightly increased. This finding probably was affected by the enough activation energy of iron(II) adsorption at that temperature. All data in Figure 7 were calculated using the Langmuir equation to obtain the adsorption capacity.

Adsorption capacity for LDH was shown in Table 1. As previously mentioned, that stability of iron(II) toward LDH at a higher temperature then adsorption capacity was decreased at 60-70 °C for both Ca/Al LDH and intercalated Ca/Al LDH due to the maximum activation energy was achieved. The results in Figure 7 and data in Table 1 also shows intercalated Ca/Al LDH has higher adsorption capacity than Ca/Al LDH at all temperatures. Thus, intercalated Ca/Al LDH gave substantial effect toward increasing adsorption iron(II) from aqueous solution.

Table 1. Adsorption capacity of LDH

Adsorbent	Temperature (°C)	Adsorption Capacity ×10 ⁻³ (mg.g ⁻¹)
Ca/Al LDH	30	1.78
	40	7.04
	50	11.16
	60	6.03
	70	4.97
Intercalated Ca/Al LDH	30	8.76
	40	9.70
	50	11.93
	60	6.49
	70	5.69

4. Conclusion

Ca/Al LDH was successfully intercalated using Keggin ion [α-SiW₁₂O₄₀]⁴⁻. X-ray diffraction result indicated that the Keggin ion was diagonally intercalated onto Ca/Al LDH interlayer space since there is a change on the diffraction at 20° after intercalation. Furthermore, FT-IR spectra of the intercalated Ca/Al LDH also exhibited a vibration peak at 1380 cm⁻¹ which indicated that the Keggin ion was inserted onto interlayer space of Ca/Al LDH. The result of iron(II) adsorption onto pristine and intercalated Ca/Al LDH showed that intercalated Ca/Al LDH has higher adsorption reactivity than its pristine form. In accordance with that results, intercalated Ca/Al LDH exhibited higher adsorption capacity toward iron(II) than the original Ca/Al LDH.

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